PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H01M 8/10, 8/02

A1

(11) International Publication Number: WO 99/13522

(43) International Publication Date: 18 March 1999 (18.03.99)

(21) International Application Number: PCT/AU98/00719

(22) International Filing Date: 4 September 1998 (04.09.98)

(30) Priority Data:
PO 8978 5 September 1997 (05.09.97) AU

(71) Applicant (*for all designated States except US*): CERAMIC FUEL CELLS LIMITED [AU/AU]; 170 Browns Road, Noble Park, VIC 3174 (AU).

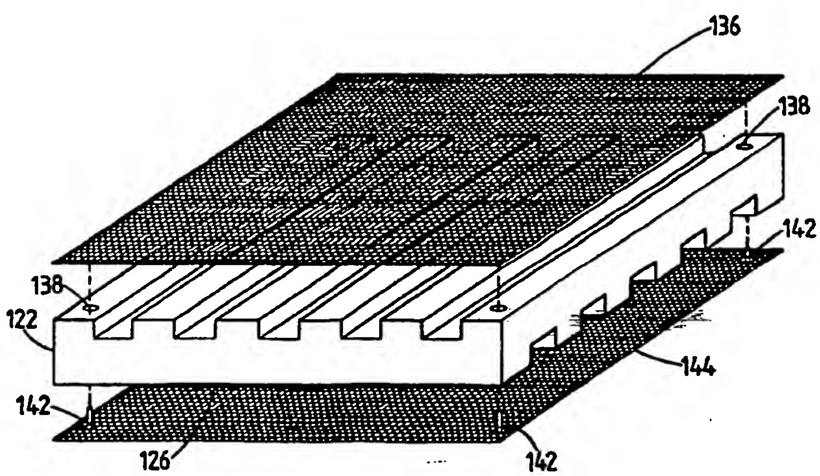
(72) Inventor; and
(75) Inventor/Applicant (*for US only*): JAFFREY, Donald [AU/AU]; 2 Bonnieview Road, Mount Dandenong, VIC 3767 (AU).

(74) Agents: HUNTSMAN, Peter, H. et al.; Davies Collison Cave, 1 Little Collins Street, Melbourne, VIC 3000 (AU).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: ELECTRICAL CONDUCTIVITY IN A FUEL CELL ASSEMBLY



(57) Abstract

A solid oxide fuel cell assembly has a gas separator plate (122) and a silver electrically conducting layer (136) disposed between the gas separator plate (122) and the cathode layer of the fuel cell. In one embodiment, the silver layer (136) is in the form of a mesh or other sheet which permits oxygen-containing gas in the oxygen-containing gas channels access through the silver layer (136) to the cathode layer. The silver layer (136) abuts heads (138) of electrically connecting links (142) through the gas separator plate (122) to pass electric current collected by the silver layer (136) to a nickel mesh (144) the anode side of the plate. The gas separator plate (122) has an alumina layer on the cathode side and may be formed of stainless steel. The silver may be at least substantially pure or alloyed, or it may be present as an intermediate compound or as a composite material with a non-metal. The silver layer may be formed on a substrate material such as stainless steel.

12:17:30

ELECTRICAL CONDUCTIVITY IN A FUEL CELL ASSEMBLY

The present invention relates to a solid oxide fuel cell assembly comprising one or more planar fuel cells and is particularly concerned with collecting electricity in such an assembly.

The current design of solid oxide planar fuel cell assemblies requires that the electric current generated in the electrolyte of a fuel cell be conducted away by a gas separator between adjacent fuel cells known as an interconnect. The gas separator must also be a good thermal conductor to conduct heat generated in the fuel cell away from the fuel cell. In some designs the interconnect is manufactured from a ceramic material which is electrically conducting at the operating temperatures while in other designs the interconnect is manufactured from a metallic material which is also a current carrier. Whatever the material of construction of the interconnects, it is essential that it be a good current carrier at the operating temperature and that the interfaces between the interconnect and the electrolyte also be conducting, i.e. the interconnect - cathode layer interface and the interconnect - anode layer interface. These requirements have proved to be difficult ones to meet in practical fuel cell designs without some compromises of the other properties.

It has proved difficult to avoid the various materials of the fuel cell assembly and the interfaces between them degrading or changing substantially during the life of the fuel cell, in so far their electrical conductivity is affected, because of the tendency of dissimilar materials to interact at the high temperatures which are required for efficient operation of a solid oxide fuel cell. For example, most metallic interconnects contain substantial quantities of the element chromium which is used to impart oxidation resistance to the metal as well as other properties. It has been found that where chromium is present in more than minute quantities it may combine with oxygen to form highly volatile oxide or oxyhydroxide gases under conditions which are typical of those experienced in operating solid oxide fuel cells. These volatile gases are attracted to the cathode-electrolyte interface where they may react to form compounds which are deleterious to the efficiency of the fuel cell. If these chromium reactions are not eliminated or substantially inhibited, the performance of the fuel cell

expensive, not very robust physically and, because of their brittle nature, require a close matching of mating surfaces to provide satisfactory electrical contact.

According to the present invention there is provided a solid oxide fuel cell assembly comprising a planar fuel cell having a solid oxide electrolyte layer with an anode layer on one side and a cathode layer on the other side, the fuel cell being disposed between a first thermally conductive heat resisting metal alloy gas separator member adjacent the cathode layer and a second thermally conductive heat resisting metal alloy gas separator member adjacent the anode layer, oxygen containing gas passages being provided between the cathode layer and the first gas separator member and fuel gas passages being provided between the anode layer and the second gas separator member, wherein a layer of electrically conductive material is provided between the cathode layer and the first gas separator member in electrical contact with the cathode layer to conduct electrical current away from the cathode layer, said electrically conductive layer being adapted to permit the oxygen-containing gas in the oxygen-containing gas passages to contact the cathode layer and comprising silver, and wherein the first gas separator member has a layer of alumina adjacent the layer of electrically conductive material.

By the invention, the electrical current is conducted away from the fuel cell via an electrically conductive layer comprising silver positioned between the alumina layer on the first gas separator member and the cathode layer of the fuel cell. We have surprisingly found that notwithstanding the relatively low melting temperature of silver, the electrically conducting layer can continue to provide efficient current collection over extended periods even at the elevated operating temperatures of high temperature solid oxide fuel cells.

The silver may be alloyed with one or more other noble metals and/or with one or more non-noble metals or may be present as an intermetallic compound or as a composite material with a non-metal in which case the silver is preferably present as a major component of the alloy, compound or material, for example at least about 50 wt% and the other component(s) should not contaminate the fuel cell. However, the electrically conductive layer advantageously

When the electrically conductive layer is formed on a substrate, the silver material may have a thickness of at least about 10 μm and may be formed on an expanded substrate mesh or other perforated sheet, advantageously formed of a metallic material such as stainless steel. The electrically conductive layer may have a thickness of 100 μm or more as described above, but preferably in the range about 20-50 μm. As a generality, the thickness of the substrate is not of concern, but usually it will be of the order of about 0.5 to 1.5 mm or less. A layer of alumina or other dense material, for example having a thickness in the range of about 1 to 5 μm or less, may be formed between a stainless steel substrate and the electrically conductive layer to prevent egress of chromium or other contaminants in the stainless steel. The stainless steel is preferably self-aluminising so that an alumina layer grows beneath the metallic conductive layer, but alternatively it may be of grade 446 or, for example, some other stainless steel containing low levels of aluminium such as is described below in which case any alumina or other dense layer would have to be applied.

Alternatively, for example, a mesh may be woven or otherwise formed from thread or other filaments of the silver material or of a substrate material such as one of the aforementioned stainless steels. The substrate material may be coated with the silver material before or after the mesh is formed. The thickness of the silver material may be as described in the immediately preceding paragraph.

The thickness and material of construction of each gas separator member are chosen to facilitate the transfer of heat across or along the gas separator members and away from the fuel cell. Each gas separator member may also provide the structural strength and rigidity of the fuel cell assembly.

By the present invention, the alloy of the gas separator members may be chosen to provide excellent and long term resistance to high temperature exposure in reducing and oxidising atmospheres without regard to the need to maintain electrical contact at the cathode layer interface at the operating temperature of the fuel cell assembly. Materials which develop, or which may be treated to develop, an alumina layer which inhibits or prevents the ingress of

separator member or, for example, the fuel gas passages may be as described in our co-pending International Patent Application PCT/AU98/00437.

Similarly with the second gas separator member, the fuel gas passages may be defined in channels formed on the anode-facing surface thereof or, for example, as described in the aforementioned International patent application PCT/AU98/00437. If the fuel cell is one of several in a stack, the second gas separator member may advantageously have an alumina layer on the cathode-facing surface and a layer of electrically conductive silver material between the cathode layer of an adjacent fuel cell and the cathode-facing surface of the second gas separator member in electrical contact with said cathode layer to conduct electrical current away from the cathode layer, the electrically conductive layer being such as to permit gas in the oxygen-containing gas passages of the second gas separator member to contact the cathode layer of the adjacent fuel cell. Thus, preferably, each fuel cell assembly in a fuel cell stack is in accordance with the present invention.

The silver material conductive layer may be electrically connected to the anode side of the first gas separator member, or to an external circuit if it is a terminal or end gas separator member, via the gas separator member itself or via an independent circuit, for example an external bus bar. If the conductive layer is electrically connected via the gas separator member itself, the body of the alloy gas separator member may be electrically conductive and/or may have an electrically conductive element extending through it. The connection of the conductive layer to the independent circuit or to or through the first gas separator member may be by means of a wire or rod, preferably of thicker cross-section than the conductive layer, of a suitable material which does not act as a source of contamination of the fuel cell. This material may be silver or some other material. The wire or rod may be welded to or simply in contact with a portion of the first gas separator member which is left free of the alumina layer. The wire or rod may be welded to a further wire or other connecting link which is attached to the anode side of the first gas separator member. The connecting link should have resistance to the gaseous fuel environment on the anode side and to adverse reactions with fuel cell materials, a suitably high melting point and high electrical

sandwiched between a pair of gas separator plates 20 and 22 which in use are in face to face contact with the anode 16 and cathode 18 respectively.

The gas separator plates 20 and 22 shown in Figure 1 are identical with an array of gaseous fuel channels 24 extending across the underside 26 and an array of gaseous oxidant flow channels 28 extending across the top side 30. The channels 24 and 28 are shown extending at right angles to each other but they may extend parallel and the respective gas flow directions may then be the same or opposite depending upon the manifolding arrangements. By providing the gas flow channels on both sides, the gas separator plates 20 and 22 may be used to form a fuel cell stack in which an identical fuel cell 12 overlies the gas separator plate 20 and another identical fuel cell 12 underlies the gas separator plate 22. Further identical gas separator plates may then be placed adjacent the opposite sides of the further fuel cells, and so forth to build up a fuel cell stack of the desired number of fuel cells. The gas separator plates provided at the ends of the stack need only have one of the arrays of gas channels, gas channels 24 for the gas separator plate at the top of the stack as described and gas channels 28 for the gas separator plate at the bottom of the stack as described. Likewise in a fuel cell assembly comprising only a single fuel cell 12 the proposed gas separator plates need only have the respective array of gas channels on the face in contact with the fuel cell. These end gas separator plates are commonly termed end plates.

In use, the gaseous fuel and oxidant flows must be kept apart and suitable manifolding (not shown) is provided to ensure this. In the cross flow arrangement illustrated this is conveniently provided by an inert cylindrical or other sleeve (not shown), for example of ceramic, which extends around the fuel cell stack with its axis normal to the gas flow channels 24 and 28 and with the corners 32 of the fuel cells 12 and the corners 34 of the gas separator plates sealed in contact with the annular inner surface of the sleeve. The fuel cell assembly is completed by terminals on the top and bottom end plates for attachment of the fuel cell or fuel cell stack to an external load.

As noted already, the fuel cell assembly 10 illustrated in Figure 1 is known and in the

separator plate 22 from the cathode side 30 through the alumina surface layer into the stainless steel substrate material, on opposed sides of the gas flow channels 28. The grooves 40 are not protected by the alumina layer. The collector rods 38 were formed of palladium but are more preferably platinum or an 80 wt% platinum 20 wt% rhodium alloy. The welds or other connections between the silver mesh and the collector rods are disposed in the grooves 40 and the grooves are sealed by means of a highly viscous glass with the collector rods 38 in electrical contact with the stainless steel substrate of the gas separator plate. The glass protects the connections between the silver and the collector rods and also protects the grooves 40 from exposure to the oxygen-containing gas. The glass may be rendered electrically conducting by loading with fine metallic powders.

Thus, the silver mesh 36 may in a multi-fuel cell stack be in contact with the anode side 26 of the gas separator plate 22. However, in the embodiments tested only a single fuel cell was used and the gas separator plate 22 must be connected to an external electrical circuit. In the embodiment tested, the gas separator plate 20 (see Figure 1) is formed of the same ferritic stainless steel as gas separator plate 22 and has a nickel mesh layer welded to the anode side of the plate.

Referring to Figure 4, a gas separator plate 122 has a construction generally the same as gas separator plate 22 shown in Figure 2. However, a conducting layer 136 is in the form of a woven mesh made from high temperature stainless steel as described above which is silver plated. This mesh is electrically connected to the cathode side of the plate 122 by way of its corners contacting four slightly raised contacts 138. The contacts 138 are the silver plated heads of electrically conducting rivets which pass completely through the thickness of the plate 122 and therefore through an alumina layer formed on the cathode side of the plate. On the anode-facing side 126, the opposite-facing rivet heads 142 are nickel or nickel plated and these clamp a nickel or nickel plated conducting mesh 144 to the anode-facing side of the plate 122. In operation of the fuel cell shown in Figure 4 the mesh 144 is pressed against the anode side of a fuel cell to make electrical contact therewith. The conduction path thus extends from the cathode side of a first fuel cell to mesh 136, then through the gas separator

During the start-up phase at period 201 the open cell voltage was 1.31 V in dry hydrogen and for period 202 it was 1.09 V in the 4% wet hydrogen. The stack operated in subsequent period 203 (for approx 100 hours) at 100 mA/cm^2, for period 204 (approx 35 hours) at 150 mA/cm^2 and for period 205 (approx 850 hours) at 200 mA/cm^2. The maintenance of a cell voltage above 0.63 V, and the low rate of degradation in performance over the latter portion of period 203, shows an improved performance over alternative constructions.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

7. A fuel cell assembly according to claim 6 wherein the mesh is in a form selected from the group consisting of woven and expanded metal.

8. A fuel cell assembly according to claim 1 wherein the electrically conductive layer is applied as a porous coating to one or both of the first gas separator member and the cathode layer.

9. A fuel cell assembly according to claim 1 wherein the electrically conductive material is applied as a coating to a substrate disposed between the first gas separator member and the cathode layer.

10. A fuel cell assembly according to claim 9 wherein the substrate is a mesh in a form selected from the group of expanded metallic material and woven.

11. A fuel cell assembly according to claim 9 wherein the substrate is stainless steel.

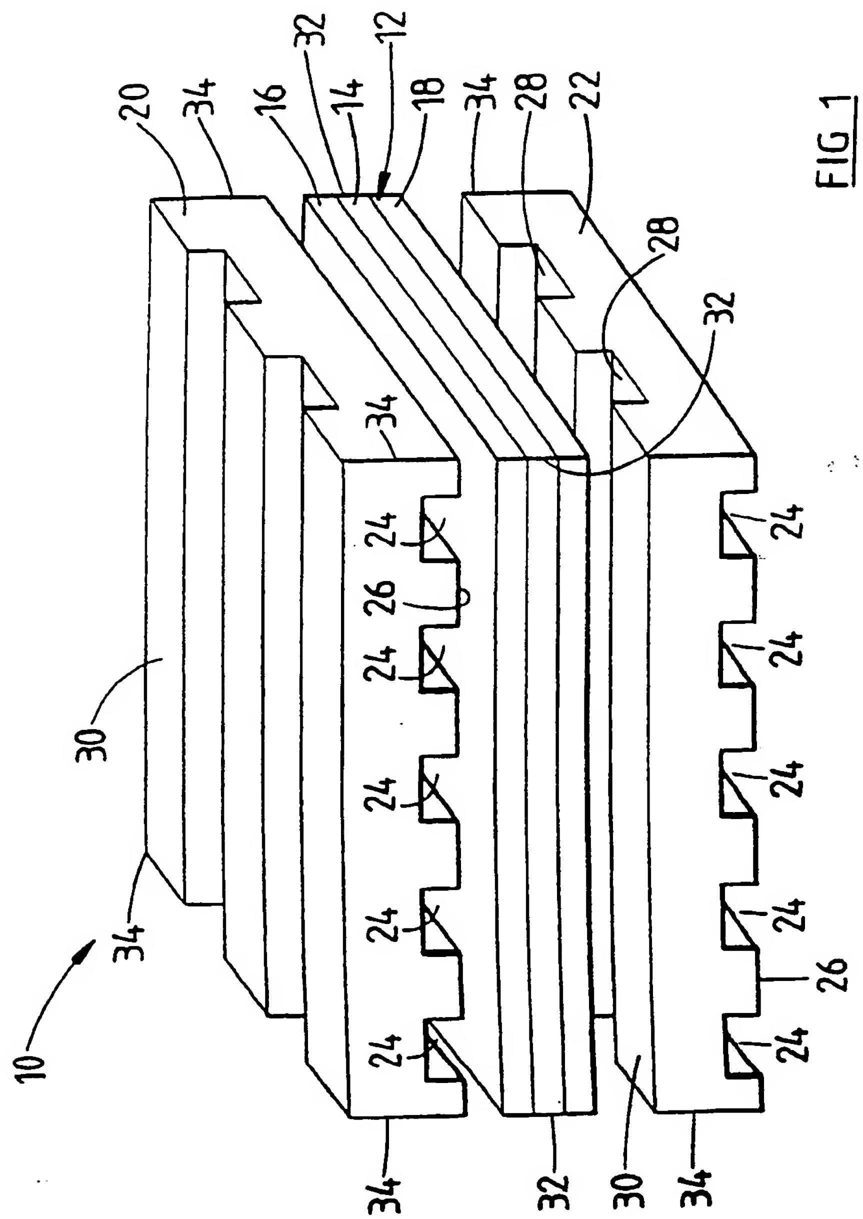
12. A fuel cell assembly according to claim 11 which includes a layer of alumina between the stainless steel of the substrate and the coating.

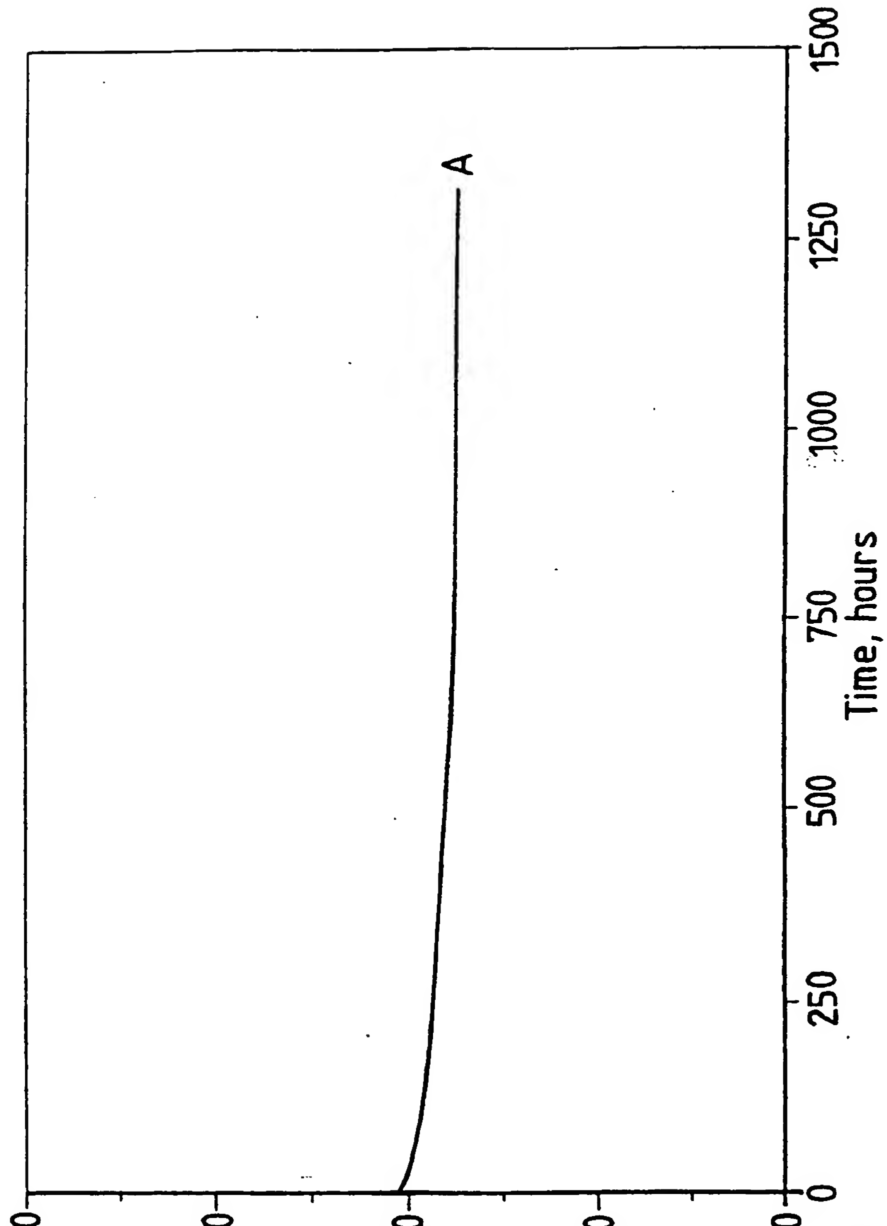
13. A fuel cell assembly according to claim 9 wherein the coating has a thickness in the range of about 20-50 μm.

14. A fuel cell assembly according to claim 1 wherein the first and second gas separator members are formed of stainless steel.

15. A fuel cell assembly according to claim 14 wherein the stainless steel is a self-aluminising stainless steel.

16. A fuel cell assembly according to claim 1 wherein the thickness of the alumina layer is up to about 5 μm.


10
20
34
16
32
14
12
18
28
22
30
24
26
FIG 1



A
Power Density, mW.cm^{-2}
400
300
200
100
0
Time, hours
0
250
500
750
1000
1250
1500

FIG 3

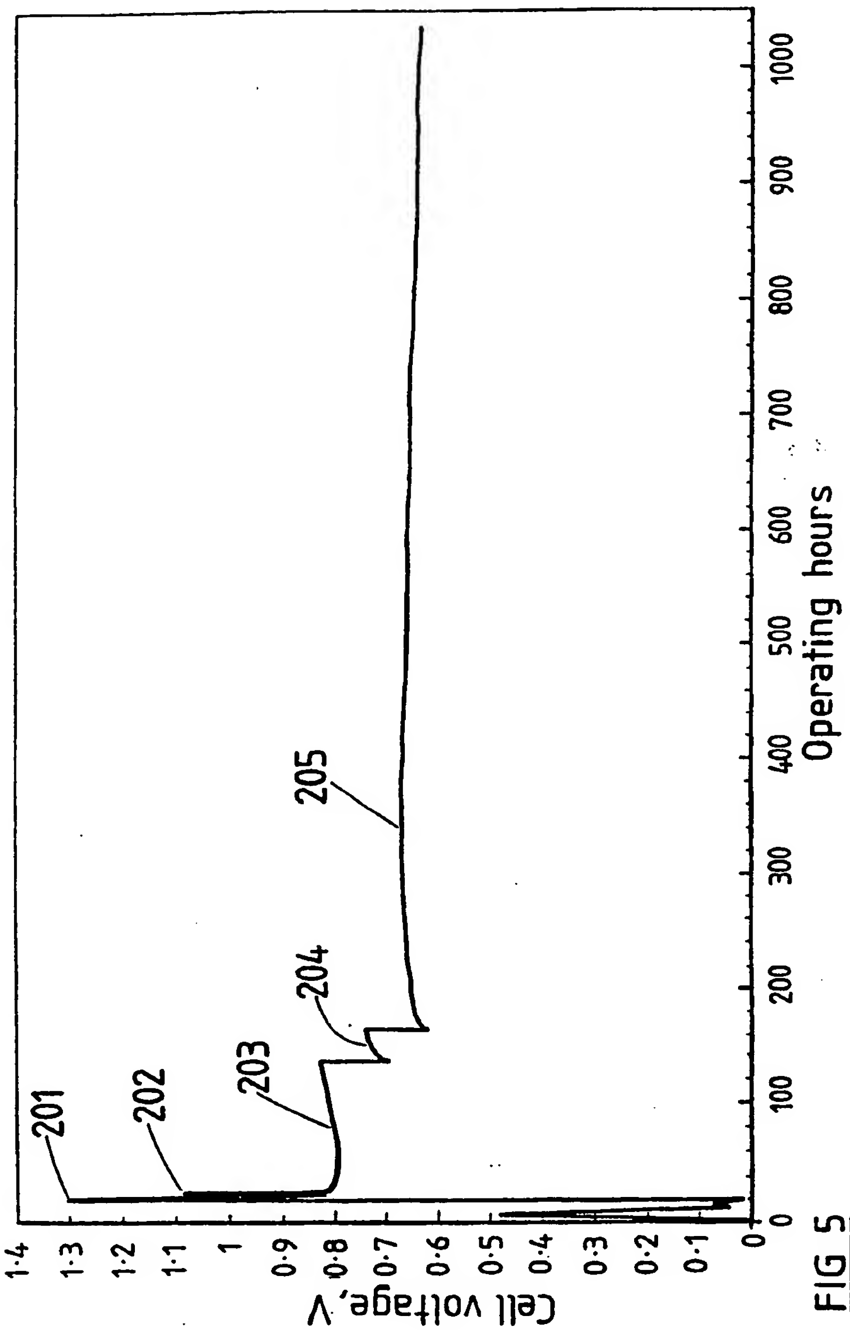

Cell voltage, V
Operating hours
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1
1·1
1·2
1·3
1·4
100
200
300
400
500
600
700
800
900
1000
201
202
203
204
205

FIG 5

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent Abstract Accession No. 92-137314/17, Class X16, JP 04079163 A (FUJI ELECTRIC MFG KK) 12 March 1992 Abstract	1-20